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The crystal structure and properties of a number of urea cocrystals are studied with regard to symmetry of the hydrogen-bonded molecular assemblies. The logical consequences of hydrogen bonding interactions are followed step-by-step. The problems of aggregate formation, nucleation, and crystal growth are also elucidated. Endeavor is made to envisage the 2-D and 3-D hydrogen bond network in a manageable way by exploiting graph set short hand. Strategies of how to control the symmetry of molecular packing are still to be elaborated. In our strategy, the programmed self-assembly has been based on the principle of molecular recognition of self- and hetero-complementary functional groups. However, the main focus for pre-organizational control has been put on the two-fold axis estimator of the urea molecule.

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Technical Report #22

"Engineering Solid-State Materials. Strategies for Modeling and Packing Control of Molecular Assemblies into 3-D Networks"

by

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The concept of hydrogen bonding as a specific interaction paved the way for synthetic receptor synthesis and programmed self-organization and supramolecular synthesis based upon the recognition of the hydrogen bond active sites of two or more subunits. The nature of any newly obtained species will depend upon the information stored in the parent compounds. Molecular engineering approaches to the synthesis of new organic solid state materials may replace techniques such as microlitography and vapor deposition.

The goals of our studies are:

Control over the symmetry of molecular assemblies in three dimensional structures through control over the site-symmetry of molecular self- and/or hetero-aggregates.

Control and optimization of the orientation of charge transfer axes toward optical directions in the crystals for NLO applications.

Among the symmetry elements determining the space groups in organic molecular crystals, the inversion center plays a pivotal role. Indeed, its absence is an absolute prerequisite toward nonlinear effects. Thus, we have undertaken the effort to examine systematically the relationships between the molecular and crystalline symmetry. In order to clarify these relationships, the following notation will be used: small letters will represent molecular point group types, capital letters crystal point group types.

Type **a** (or **A**) denotes the presence of direct rotation axis only.

Type **m** (or **M**) denotes the presence of mirrors (plane of symmetry) or inverse 4-rotation, and, eventually, the presence of direct rotation axis.

Type **i** (or **I**) characterizes the presence of inversion center among the group elements.

$$\mathbf{a} \Longrightarrow \mathbf{A}$$

mol. 2-fold axis	crystal 2-fold axis

$$\mathbf{m} \Longrightarrow \mathbf{M}$$

mol. mirror plane	crystal planes of symmetry

In our design effort, we seek to replace the inversion center I in the crystal for another symmetry element A or M.

For
Codes
and/or
Special
A-1

Results:

Our specific goals are to design and synthesize urea based cocrystals in which the twofold symmetry and hydrogen bond characteristics of the urea molecule guide the self-organization into noncentrosymmetric motifs. The two-fold symmetry, bifunctionality and high density of hydrogen bonds make the urea molecule ideal for the approach as these factors may override the influence of dipolar forces which tend to favor centrosymmetric lattices.

Figure 1 depicts the unique structural aspects and symmetry of the urea molecule: urea is bi-functional, i. e., it can serve as both proton donor and proton acceptor. It is flat and possesses a 2-fold axis and a mirror plane, and contains four proton donor sites and one oxygen accepting site. However, the oxygen site can accept up to four hydrogen bonds arranged with local C_{2v} symmetry. The hydrogen bond acceptor and donor sites are sterically accessible and can provide a directing influence over the aggregate symmetry.

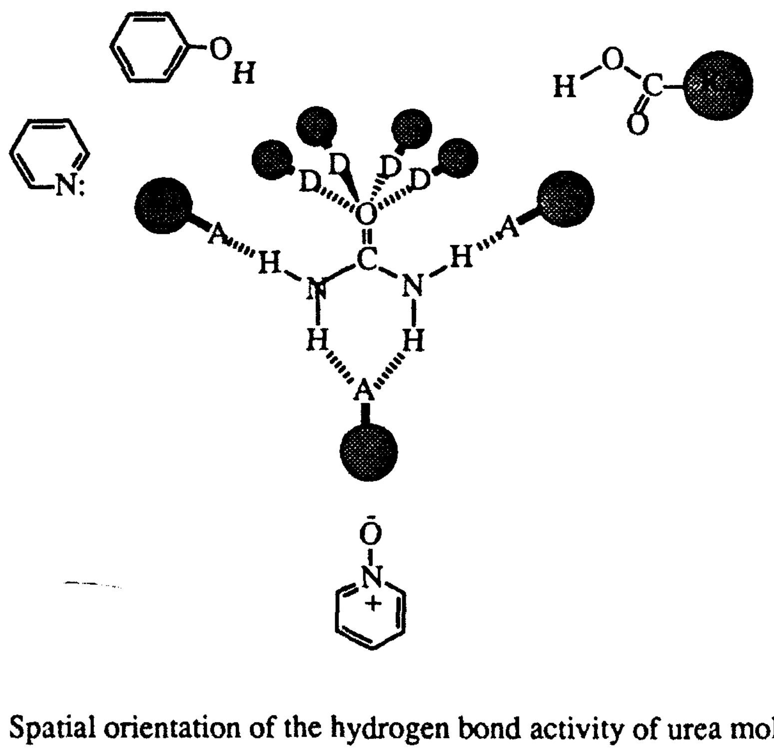
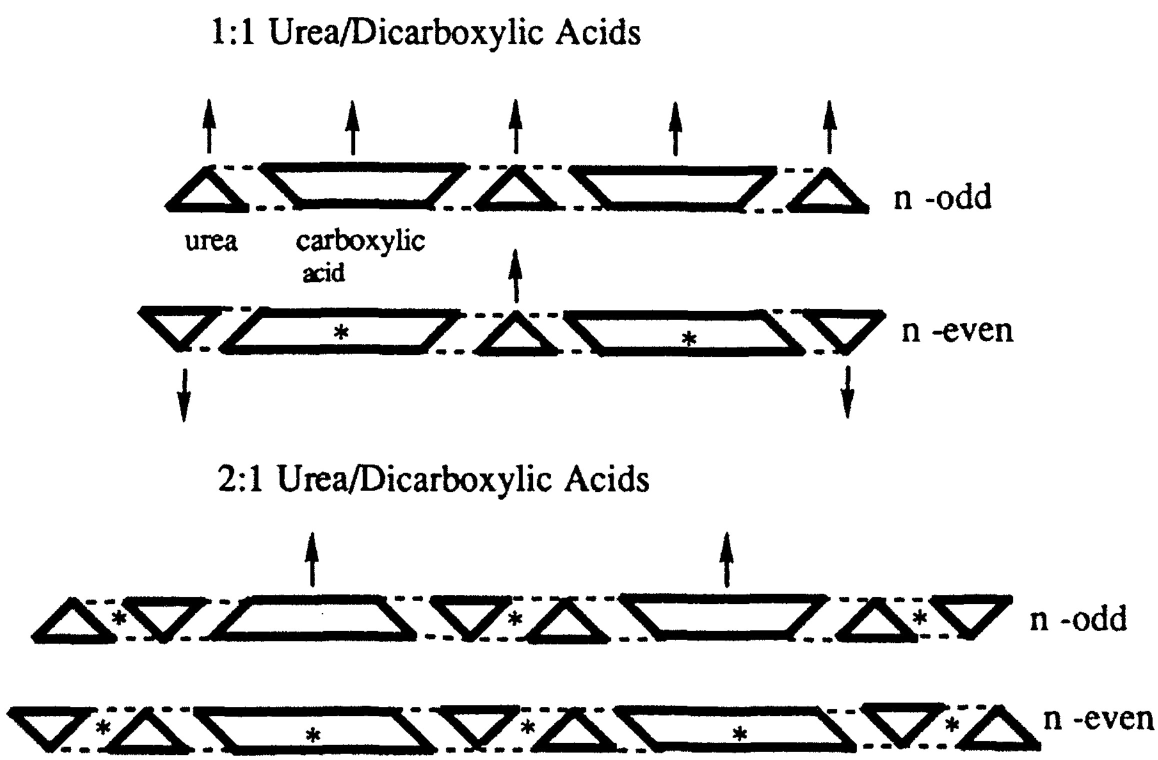


Fig. 1. Spatial orientation of the hydrogen bond activity of urea molecule

We have synthesized and studied the structures of 10 cocrystals of urea with dicarboxylic acids:

Urea/Succinic - (2:1)
Urea/Maleic - (1:1), (1:2) and (2:1) cocrystals
Urea/Fumaric - (2:1)
Urea/Glutaric - (1:1) and (2:1) cocrystals
Urea/Adipic (1:1) and (2:1) cocrystals
Urea/Azelaic (1:1) and (2:1) cocrystals
The most important structural data are collected in Tables 1, 2 and 3.

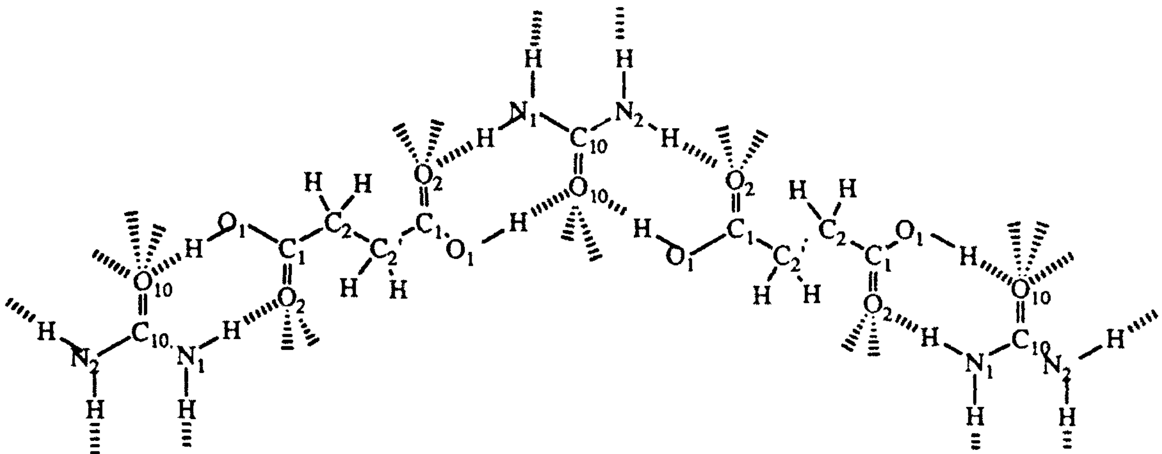
As shown in scheme 1 the symmetry of the aggregate chains is controlled by the symmetry of the urea molecule, the number of carbon atoms in the acid chain (odd, even), and the stoichiometric ratio of the parent compounds. The only case where no inversion center is introduced into aggregate chains is in the 1:1 urea/dicarboxylic acid complex, in which the acid has an odd number of carbon atoms.



Scheme 1. Symmetry control in urea/dicarboxylic acid hetero-aggregate chains

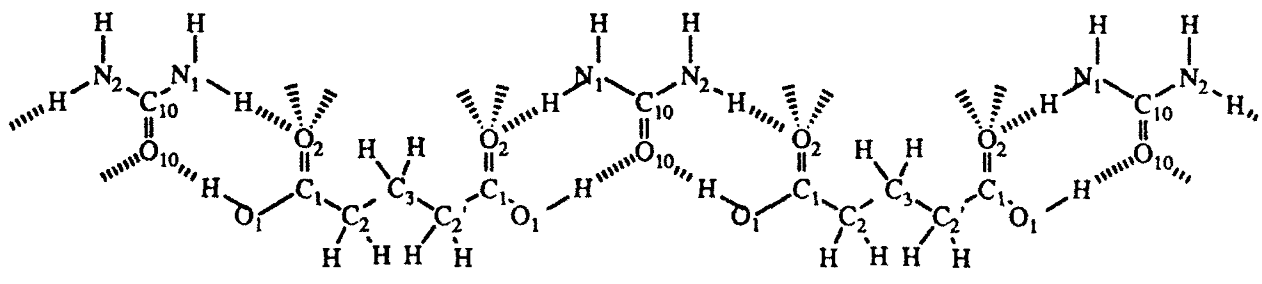
Scheme 2 and 3 depict the hydrogen bond motifs of the heteroaggregates in 1:1 urea/dicarboxylic acids with n- odd or even number. Only two accepting and two donating abilities of urea are used to form polar chains. However, as it was already mentioned, urea is capable of accepting 4 donors and 4 acceptors. These additional hydrogen bond capabilities are used in order to form 2-D and 3-D networks (see Fig 2, 3), which are not necessarily acentric.

n = even



Scheme 2. Hydrogen bond connectivity pattern in heteroaggregate 1:1 urea/succinic acid

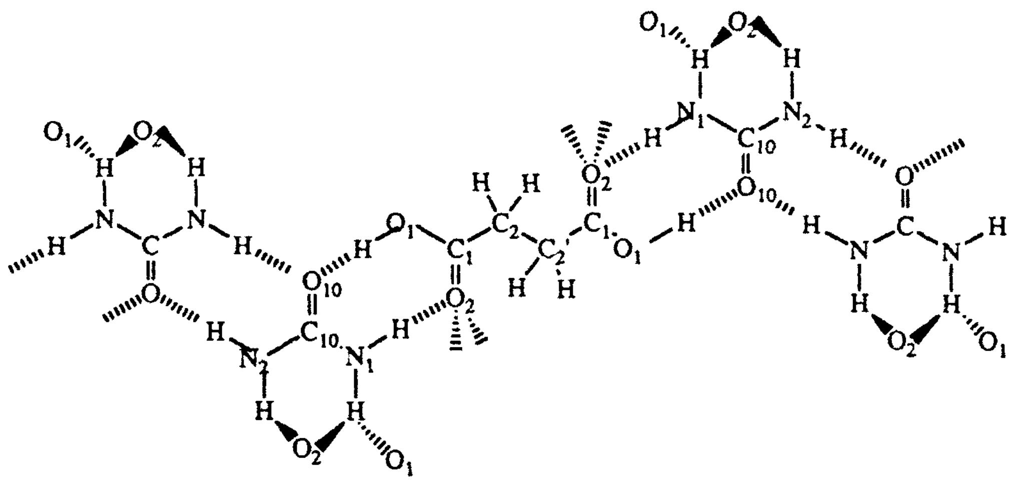
n = odd



Scheme 2 Hydrogen bond connectivity pattern in hetero-aggregate 1:1 urea/glutaric acid

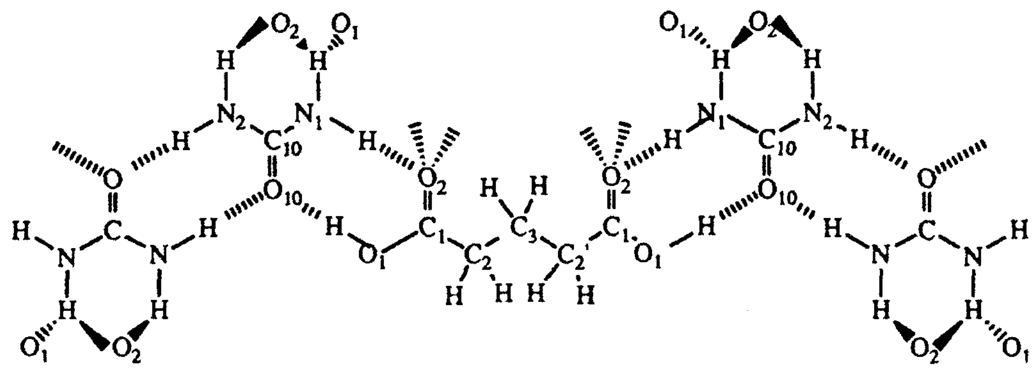
Schemes 4 and 5 depict the connectivity pattern of the hydrogen bonded hetero-aggregates (chains) in 2:1 urea/dicarboxylic acids extended to next hetero-aggregates (chains) to form 2-D and 3-D hydrogen bonded networks. In all crystals with n-odd number of carbon atoms, the hydrogen bonded chains assemble into 2-D layers (fig.2). However in cocrystals with n-even number of C-atoms, the hydrogen bonded chains are arranged in a complex 3-D networks (fig 3).

n = even



Scheme 5. Hydrogen bond connectivity pattern in hetero-aggregate 2:1 urea/succinic acid

n = odd



Scheme 6. Hydrogen bond connectivity pattern in hetero-aggregate 2:1 urea/glutaric acid

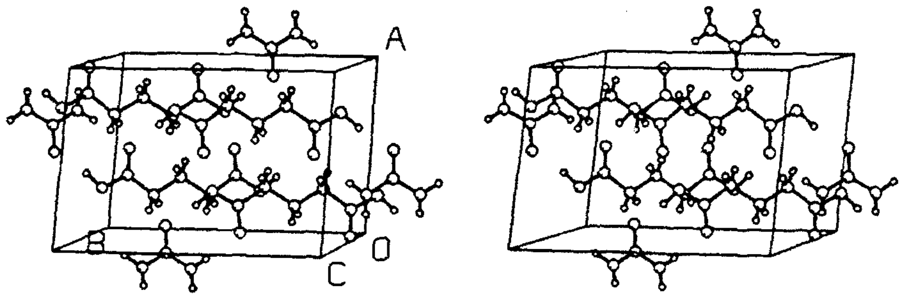


Fig. 2a Stereoview of the unit cell of 1:1 urea/glutaric cocrystal.

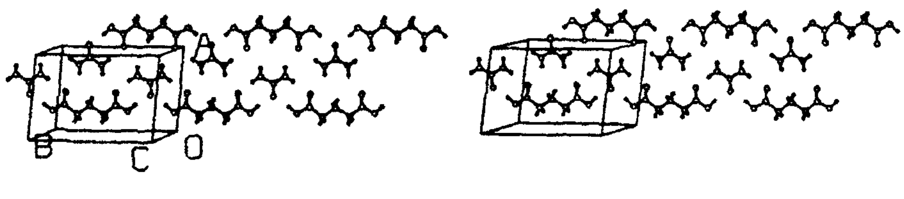


Fig. 2b Stereoview of the two dimmensional molecular layer depicting the hydrogen bond connectivity patterns in 1:1 urea/glutaric acid cocrystal

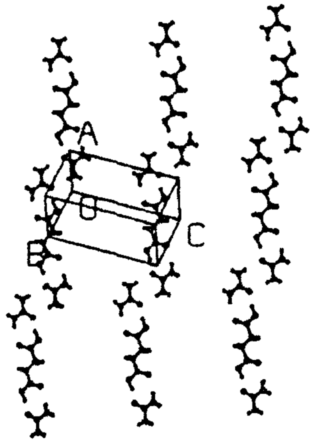


Fig. 3a. Two dimmensional hydrogen bond connectivity patterns in 2:1 urea/succinic acid cocrystal.

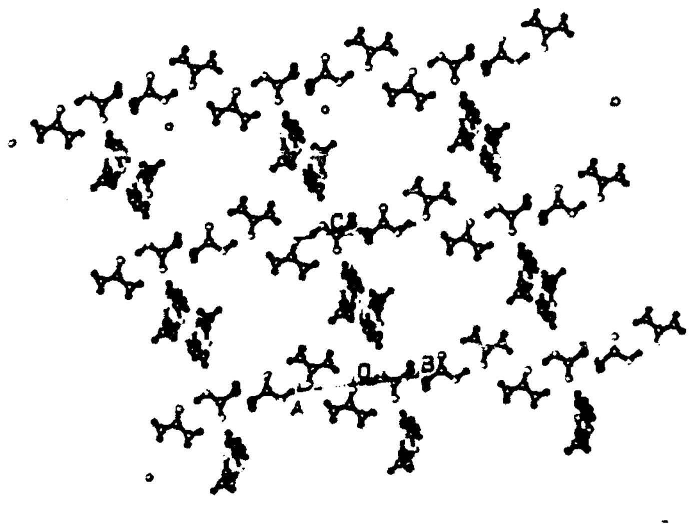


Fig 3b. Three dimmensional hydrogen bond connectivity patterns in 2:1 urea/succinic acid cocrystal.

Interesting class of cocrystals appear to be the urea complexes with maleic acid. We have synthesized and characterized by FTIR and NMR and melting points three different cocrystals (1:1, 1:2 and 2:1 urea/maleic acid) (fig 4, 5). The weak C-H...O and C-H...N bonds play significant role for stabilizing the structure of those crystals. Each two hydrogen bonded molecular hetero-aggregates (1:2 urea maleic acid) form a centrosymmetric super-aggregate through weaker N-H...O bonds, which in turn are combined through numerous C-H...O bonds into a nonpolar molecular sheets. In the 1:1 complex the strongest O-H...O and N-H...O interactions are used to form weakly polar chains. The y-components of urea dipole moments cancel in the 3-D networks, but the x- and z- components are non-zero. The chains are connected into polar sheets by weaker N-H...O bonds. Additional weak C-H...O bonds control the molecular forces between the sheets. This fact is very likely to be decisive for the noncentrosymmetric arrangement of 1:1 urea/maleic acid molecular aggregates in a noncentosymmetric 3-D networks.

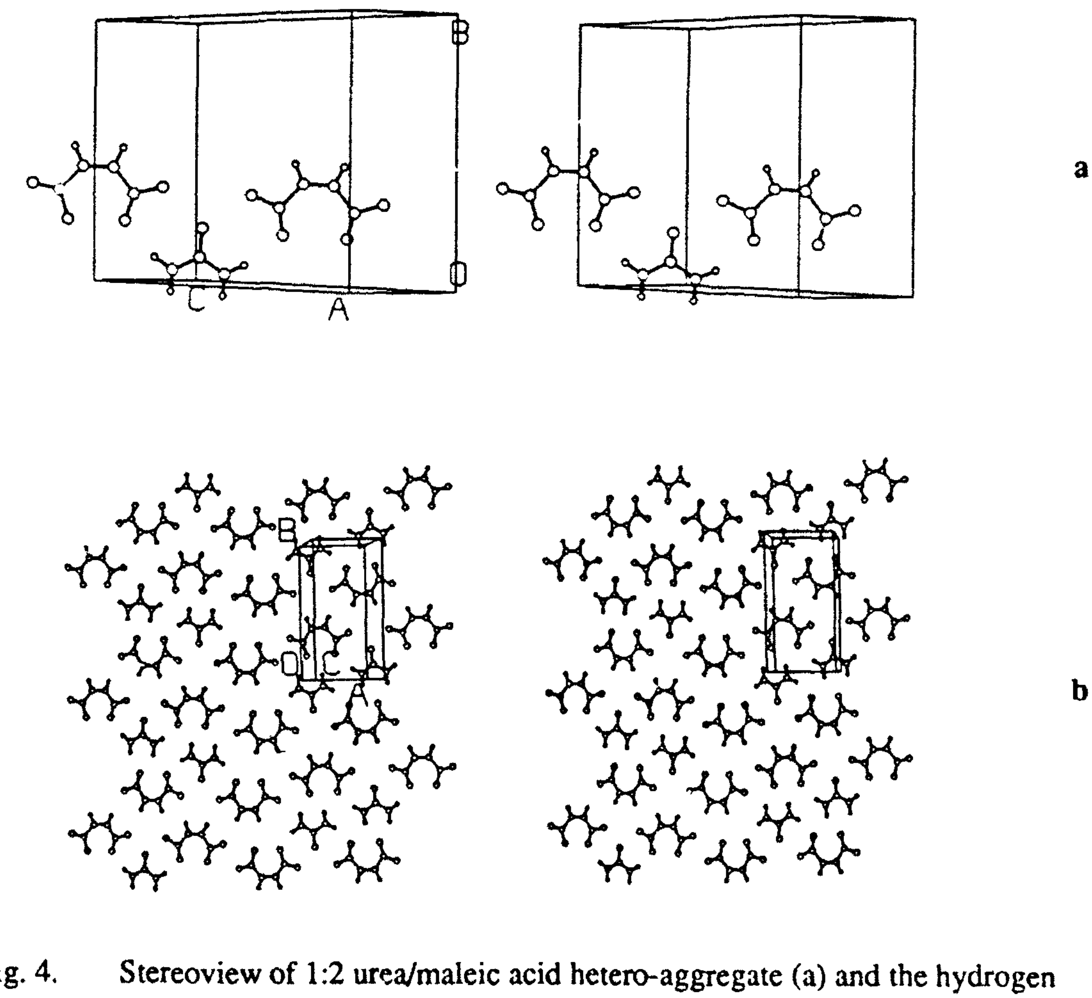
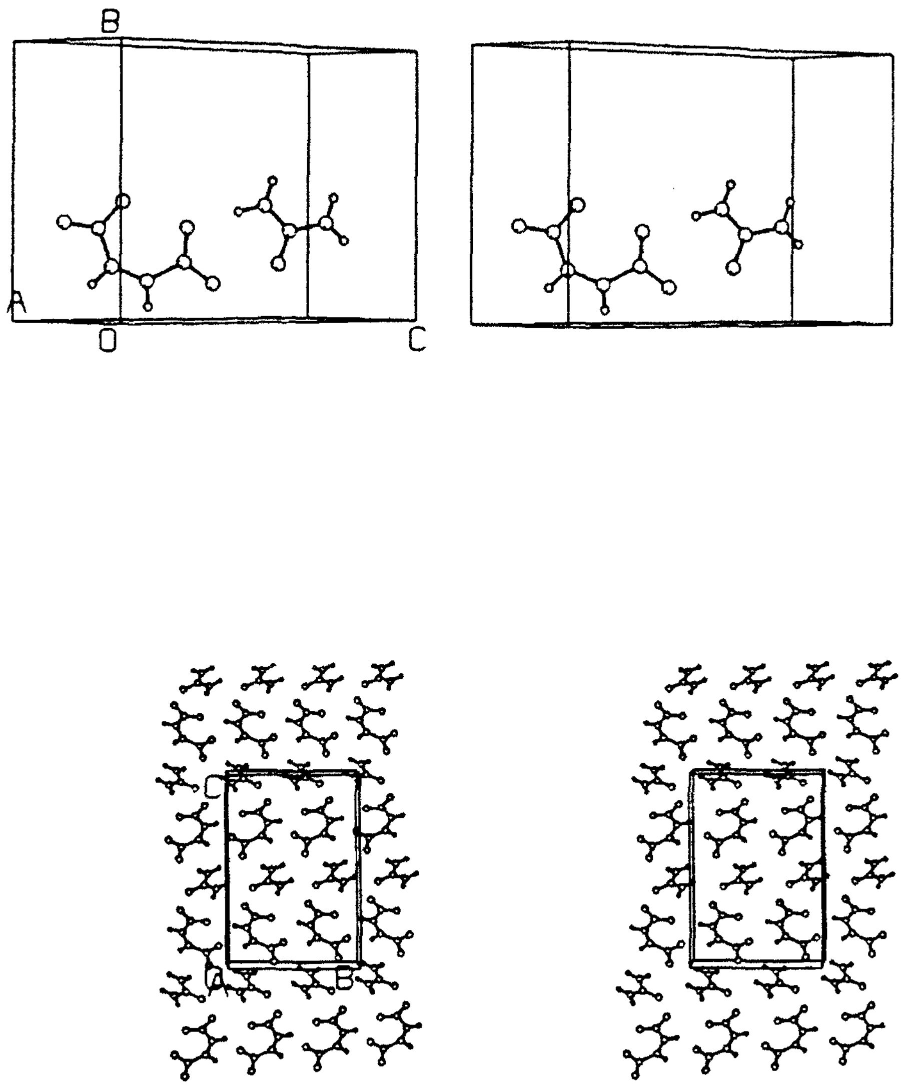


Fig. 4. Stereoview of 1:2 urea/maleic acid hetero-aggregate (a) and the hydrogen bonded molecular layer (b).



a

b

Fig. 5. Stereoview of the 1:1 urea/maleic acid hetero-aggregate (a) and the hydrogen bonded polar layer (b).

TABLE 1 Crystal lattice parameters for 2:1 Urea/Dicarboxylic acid cocrystals

	Ur/Succinic	Ur/Fumaric	Ur/Glutaric	Ur/Adipic	Ur/Azelaic
Space Group	$P2_1/c$	$P2_1/c$	C2/c	$P2_1/c$	C2/c
Z (mol units)	2	2	4	2	4
a(Å)	5.637	5.545	11.954	8.307	17.890
b(Å)	8.243	8.221	10.93	7.244	11.113
c(Å)	12.258	12.443	9.078	10.989	9.685
β(°)	96.80	97.25	97.86	97.18	120.23
V($Å^3$)	565.6	562	1175	656	1664
V/Z($Å^3$)	283	281	294	328	416

TABLE 2 Crystallographic data for the most important molecular bondlengths (Å) in urea and some urea cocrystals.

Urea covalent bonds	C=O	C-N1	C-N2	N1-H_{syn}	N1-H_{anti}	N2-H_{syn}	N2-H_{anti}
Urea (RT)	1.260	1.352	1.352	1.003	0.998	1.003	0.998
Urea (*123K)	1.265	1.350	1.350	1.013	1.019	1.013	1.019
Urea/Phosphoric	1.281	1.324	1.323	1.003	1.000	1.002	1.001
Urea/Maleic (1:1)	1.293	1.317	1.317	0.959	0.946	0.928	0.959
Urea/Maleic (1:2)	1.277	1.322	1.318	0.95	0.949	0.95	0.95
Urea/Oxalic (1:1)	1.261	1.332	1.332	0.81	0.84	0.81	0.84
Urea/Oxalic (2:1)	1.260	1.318	1.321	0.88	0.84	0.86	0.86
Urea/Glutaric (1:1)	1.262	1.322	1.326	0.85	0.87	0.94	0.82
Urea/Succinic (2:1)	1.255	1.325	1.324	0.90	0.76	0.83	0.80
Urea/Fumaric (2:1)	1.255	1.327	1.326	0.89	0.85	0.88	0.80
Urea/Adipic (2:1)	1.250	1.330	1.324	0.98	0.89	0.90	0.89
Urea/Glutaric (2:1)	1.249	1.332	1.329	0.83	0.86	0.85	0.86
Urea/Azelaic (2:1)	1.248	1.326	1.323	0.91	0.78	0.85	0.79

TABLE 1 Space groups and melting points for urea/dicarboxylic acid cocrystals.

	2:1 Ur/Dicarb. Acid		1:1 Ur/Dicarb. Acid		1:2 Ur/Dicarb. Acid	
	Space group	T_m (C°)	Space group	T_m (C°)	Space group	T_m(C°)
Urea/Oxa	$P2_1/c$		C2/c		-	
Urea/Malonic	-		$P2_1/n$		-	
Urea/Succinic	$P2_1/c$		+		-	
Urea/Fumaric	$P2_1/c$		-		-	
Urea/Maleic	+		Cc	88-90	$P2_1/n$	105-108
Ur/eaGlutaric	C2/c	125-128	$P2_1/n$		-	
Urea/Adipic	$P2_1/c$	106-108	+	102-105	-	
Ur/eaPimelic	+	127-128	+	88-91	-	
Urea/Suberic	-	-	-	-	-	
Urea/Azelaic	C2/c	99-102	+	87-89	-	

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